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Single crystal of $RuSr_2GdCu_2O_8$

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Abstract

We have tried self-flux and pulsed laser deposition (PLD) method to make single crystals of $RuSr_2GdCu_2O_8$. In the self-flux method, we added the excess optimum solvent (Ru:Gd:Cu = 0.8:0.4:1.7) during growth under a low cooling rate of 1.5°C/hr. But, we could not find any single crystals. In the PLD method, we found the growth condition of single crystal phase with substrate temperature (~800 °C) and substrates ($SrTiO_3$).

Keywords: unconventional superconductor; self-flux; $RuSr_2GdCu_2O_8$; PLD; single crystal

1. Introduction

Recently, interplay of magnetism and superconductivity has attracted a great deal of interests [1-4]. Especially, the hybrid system of rutheno-cuprate compounds is particularly interesting, in which a long range magnetic ordering with a ferromagnetic component and superconductivity have been reported to coexist. One of the most interesting effects is the formation of π-states in superconductor(S)/ferromagnetic-metal(FM)/superconductor(S) (S/FM/S) Josephson junctions [5]. Under a suitable condition, the phase difference θ between two superconductors becomes π in the ground state in contrast to $\theta = 0$ in ordinary Josephson junctions without voltage. Recently, the quiet qubit based on S/F/S π-junction has been expected as a promising device to realize quantum computation, because the spontaneously generated two-level system in this structure is robust against incoherency due to external fluctuations.

In the experiments of the S/F/S junction, it is reported the phase of order parameter is shifted π by changing temperature or thickness of ferromagnetic layer between the superconductor layers [6, 7]. In the theoretical works, it is reported that the mechanism of the 0-π phase transition can be attributed to thickness-dependent phase shifts between the wave numbers in ferromagnetic-insulator (FI) layers in S/FI/S junctions [8]. This indicates a possibility of the π phase-change in the S/I/F/I/S junctions such as $RuSr_2GdCu_2O_8$ (Ru1212). Purpose of this study is to understand the relation between superconductivity and magnetism in Ru1212 by measuring the intrinsic Josephson effects and the phase shift of Cooper pairs by changing temperature, magnetic field and carrier density. To clarify the unconventional superconducting mechanism, the large and high-quality single crystals of Ru1212 are needed. An important question concerns to the electronic coupling between the magnetic and the superconducting layers, which alternate on a nano-meter scale. Relevant information can be obtained from a detailed investigation of the interlayer transport. Although it is difficult to make high quality single crystals of Ru1212, we have succeeded in growing Ru1212 polycrystalline

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crystals. This success is a very important step for following the next step of growing a large single crystal. Therefore, we have tried to make the single crystals of Ru1212.

2. Experimental

Ru1212 has a tetragonal crystalline structure with RuO_2 and CuO_2 layers separated by SrO layers. The structure forms a natural S/I/F/I/S multilayer, where "I" stands for insulating layers formed by SrO, "F" for the magnetic RuO_2 layers with a weak ferromagnetic component, and "S" for the superconducting CuO_2 layers. The reasons why growth of single crystals of this compound is difficult are that the Ru1212 melts incongruently, and that the crystals form at relatively high temperature over 1100°C where it is difficult to achieve a significant degree of solubility of Ru atoms in the crystal, because the vapor pressure becomes high and thus the escape rate of Ru is very high during the growth process of single crystal. We have investigated the crystal growth in the system Ru-Sr-Gd-Cu-O using a variety of self-solvent compositions in a flowing oxygen atmosphere.

Self-flux method is investigated and found to be useful in this work. Total weight 10 g of the mixtures of RuO_2, $SrCO_3$, Gd_2O_3 and CuO was ground in a ball mill for over 4 hours. Among the self-flux compositions, we tried to add the excess solvent composition (0.8Ru : 0.4Gd : 1.7CuO). Then, the ground mixtures were transferred into an alumina crucible and were at first decomposed at 880°C in air for two days. The incompletely-calcined mixtures were reground as powders and pressed as pellets, which were calcined at 920°C in flowing oxygen for two days, followed by cooling to room temperature. Generally, for growing single crystals, magnitude of cooling rate is important. A slow cooling rate leads to a long growth period and Ru has the high vapor pressure. We investigate the follows steps for crystal growth; (1) the calcined pellet was ground, milled, and pressed as pellets into Pt crucible, (2) heating the mixtures up to 1300°C for 2 hrs, (3) cooling down to 935°C at a rate of 1.5°C/hr, and finally (4) cooling to room temperature at a rate of 200°C/hr. The whole growth steps were carried out in flowing oxygen [9].

Pulsed laser deposition (PLD) was performed using a KrF excimer laser. The energy of laser is 120mJ and the frequency is 10 Hz. Targets were sintered pellets rotating during deposition. Target to (100) $SrTiO_3$ substrate distance was fixed to 5 cm. Deposition was carried out in high purity (5N) oxygen or the mixture of Ar and O_2 gas at a constant pressure of 0.2 Torr. The deposition chamber was evacuated to 10^{-5} mbar before the gas was bled into the system. We tried in PLD growth of $RuSr_2GdCu_2O_8$ films from the stoichiometric target. Substrate temperature was between 750 and 950 °C. Evaluation of the crystallinity of the sintered and grown samples was made by measuring X-ray (CuKα, λ = 0.15406 nm) diffraction patterns.

Fig. 1. Photographs of the pellets after the crystal growth. Pellet A is grown adding the solvent before the crystal growth and B grown adding the optimum solvent at the first mixing.

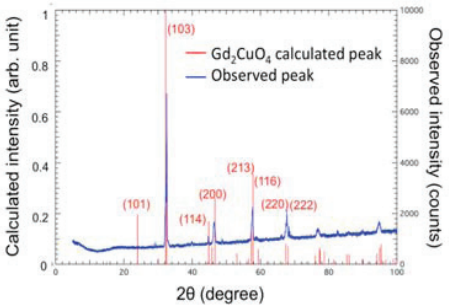


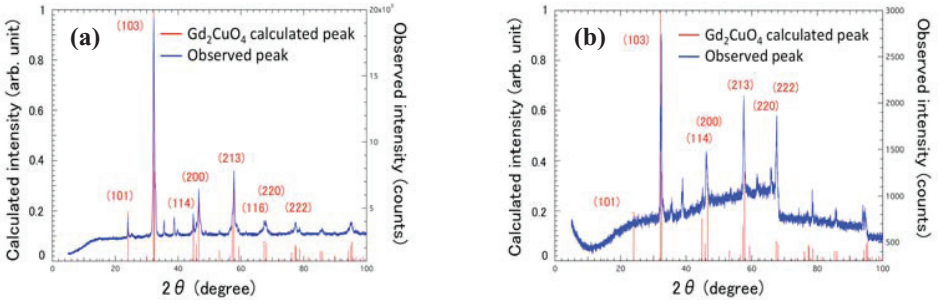
Fig. 2. X-ray diffraction pattern of the surface of pellet B, which has melted partially.

3. Result and Discussion

Figure 1 shows the photograph of the pellets after crystal growth. The left figure shows the pellet A, adding the optimum solvent at first mixing, and the right figure shows the pellet B, adding the solvent before the crystal growth. From Fig. 1, both pellets mostly do not melt and we could not find visible single crystals with optical microscope. But, there is a mark of pellets to melt on surface, such as the pellet (B). We shaved the surface to obtain the samples for XRD measurements. The spectrum of the XRD is shown in Fig. 2. The red lines indicate Gd_2CuO_4 peaks and the blue line indicates the observed peak. From Fig. 2 the spectrum consists with the profile of Gd_2CuO_4. And also, we evaluated the precursor by XRD before the single crystal growth. The XRD patterns of the precursor are shown in Figs. 3. They show that precursor also dominated with Gd_2CuO_4. From these data, before and after the crystal growth, there is no change of the main substances. Generally, for making the single crystals in flux-method, powder consisted with

single crystal on stoichiometry is needed. So, we make the powder of Ru1212 and Ru1212 powder press to the pellet as precursor. In a similar way of crystal growth, the precursor is heated to 1300 °C and cooled down slowly. Using the Ru1212 precursor, the result of crystal growth is that pellet does not melt such as the left figure in Fig. 2. After the crystal growth, we performed the XRD and showed the results in Figs. 3. From the figure, the pellet also dominated the Gd_2CuO_4. All of these pellets do not melt and this result indicates that heating temperature is low for crystal growth. In the future, we will find the melting temperature of all these pellets.

From Fig. 1, both pellets mostly do not melt and we could not find the single crystals. But, there is a mark of pellets melted on surface, such as the pellet (B). We shaved the surface to obtain the sample for XRD measurements. The spectrum of the XRD is shown in Fig. 2. The red line indicates Gd_2CuO_4 X-ray peaks and blue line indicates the observed peak. From Fig. 2 the spectrum consists with the profile of Gd_2CuO_4. And also, we evaluated the precursor by XRD before the single crystal growth. The XRD pattern of the precursor is shown in Fig. 3. It shows that precursor also dominated with Gd_2CuO_4. From these data, before crystal growth and after, there is no change of the main substances. Generally, for growing single crystals in a flux-method, a stoichiometric powder of the single crystal is needed. So, we have made the powder of Ru1212, and have pressed it into the pellet as precursor. In a similar way of crystal growth, the precursor is heated to 1300 °C and cooled down slowly. Using the Ru1212 precursor, the result of crystal growth is that the pellet does not melt such as the left figure in Fig. 1. After the crystal growth, we performed the XRD, shown in Figs. 3 (b). The pellet also dominated in the Gd_2CuO_4 peaks. All of these pellets do not melt and these results seem to be that the heating temperature is low for crystal growth. So, as a next step, we will try to find the melting temperature in all these pellets.



Figs. 3. XRD patterns of the precursor. (a) and (b) correspond to the pellet A and B in Fig.1.

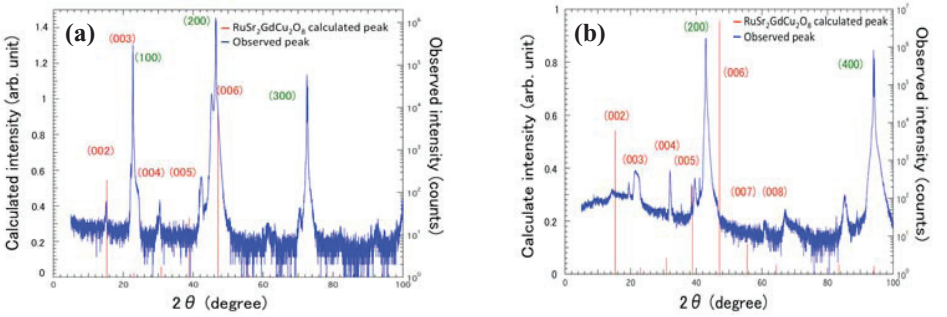


Fig. 4. X-ray diffraction patterns of the thin films made by PLD method on (a) SrTiO3 and (b) MgO substrate.
The red lines indicate the $RuSr_2GdCu_2O_8$ peak positions and green labels are the indexes of the substrates.

We have tried PLD method also to make the Ru1212 thin films using the MgO and $SrTiO_3$ substrates with the temperature range between 700 and 850 °C. Figures 4 show the patterns of X-ray diffraction with (a) $SrTiO_3$ and (b) MgO substrates. The red lines indicate the peaks of $RuSr_2GdCu_2O_8$. Green characters show the indexes from the substrates. Using MgO substrate, the peak profiles of (002) index of Ru1212 could not be found. On the other hand, in the case of $SrTiO_3$ substrate, the diffraction peaks of Ru1212 appear. But from Fig. 3(a), this film is not in single phase. The lattice parameter of Ru1212 is $a = 0.383$ nm, that of $SrTiO_3$ $a = 0.3905$ nm, and that of MgO $a = 0.4212$ nm. The lattice constant of Ru1212 is close to that of $SrTiO_3$. Then, the single crystal of Ru1212 may grow. Next we have performed PLD at several temperatures to make clear the temperature dependence of thin film growth. Figure 5 shows the XRD patterns at 720 °C, 800 °C and 850 °C. Only at 800 °C, the XRD peaks of Ru1212 emerge. These XRD results suggest that one of the conditions for Ru1212 single crystals in PLD method is achieved using $SrTiO_3$ substrate

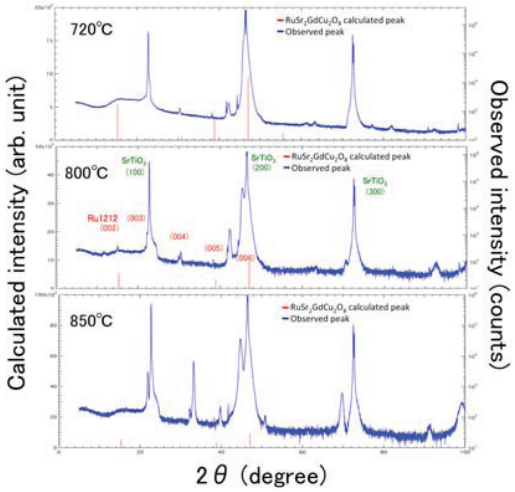


Fig. 5. Temperature dependence of X-ray diffraction pattern. Red lines indicate peak positions of Ru1212.

around at 800 °C. We will find optimum condition for single crystal growth of Ru1212, which includes dependence of the pressure and the ratio of O_2 and Ar.

Conclusion

We have tried the self-flux and pulsed laser deposition (PLD) method to grow single crystals of $RuSr_2GdCu_2O_8$. In the self-flux method, even with the excess optimum solvent (Ru:Gd:Cu = 0.8:0.4:1.7) during growth under a low cooling rate of 1.5°C/hr, we have failed to grow the single crystals. In the PLD method, we have found the growth condition of single crystal phase with substrate temperature (~800 °C) and substrates of $SrTiO_3$. The availability of single crystals is critical to many fundamental studies and understanding the nature of this fascinating class of materials which has coexistence of ferromagnetic and superconducting properties.

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